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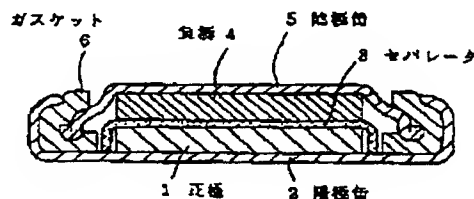
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TABUCHI JUNJI  
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NUMATA TATSUJI(54) ELECTRODE BLACK MIX AND NONAQUEOUS  
ELECTROLYTIC BATTERY

## (57) Abstract:

PURPOSE: To prepare a black mix for a battery electrode, whose electron conductivity is reduced, and provide a nonaqueous electrolytic battery whose internal resistance is reduced by the use of the black mix.

CONSTITUTION: A black mix for a battery electrode contains as positive electrode active material a manganese dioxide or lithium transition metal oxide, and as a positive electrode electroconductivity giving agent, a carbonaceous material containing carbon nanotube or carbonaceous material containing carbon nanotube including metal ions is added to this black mix. The resultant is used as a black mix for the battery electrode.

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TRANSLATION

[Title of the Invention] Battery Electrode Black Mix And  
Nonaqueous Electrolytic Battery

[What is Claimed is]

[Claim 1] A black mix for a battery electrode containing a positive electrode active material, a binder, and a conductivity giving agent, characterized in that said conductivity giving agent is a carbonaceous material containing a carbon nanotube or a carbonaceous material containing a carbon nanotube containing metallic ions.

[Claim 2] A black mix for a battery electrode according to Claim 1, wherein said positive electrode active material is a manganese dioxide or a lithium transition metal oxide.

[claim 3] A nonaqueous electrolytic battery having a black mix for a battery electrode stated in Claim 1, a negative electrode for occluding lithium, and a nonaqueous solvent electrolyte.

[Claim 4] A nonaqueous electrolytic battery according to Claim 3, wherein said negative electrode for occluding lithium is either of a carbonaceous material for intercalating or doping metallic lithium, lithium alloy, or lithium and a conductive macromolecular material.

[Detailed Description of the Invention]

[0001]

[Industrial Field of Application]

The present invention relates particularly to a black

mix for a battery electrode that the internal resistance can be reduced and a battery voltage drop caused at the time of charge or discharge is improved and a nonaqueous electrolytic battery using it.

[0002]

[Description of the Prior Art]

A lithium primary battery using metallic lithium for a negative electrode and manganese dioxide for a positive electrode is widely used. This positive electrode active material is mixed with a binder such as Teflon and acetylene black which is a conductivity giving agent so as to form a black mix for a battery electrode and put into practical use. A lithium ion secondary battery noticed as a small sealed secondary battery in recent years uses lithium cobalt oxide ( $\text{LiCoO}_2$ ) for a positive electrode and graphite or amorphous carbon for a negative electrode. The positive electrode active material in this case also uses polyvinylidene fluoride (PVDF) as a binder and graphite as a conductivity giving agent as indicated in Japanese Patent Application Laid-Open 4-249860. The aforementioned manganese dioxide and lithium cobalt oxide are excellent battery active materials, though the electron conductivity is low and the internal resistance when they are incorporated in a battery is increased unless a conductivity giving agent is mixed and they are not practical. Therefore, acetylene black is mixed as a

conductivity giving agent. Acetylene black is an excellent conductivity giving agent. However, its particle diameter is very small, so that the use of a secondary structure which is called structure such that several particles are tied in a row provides conductivity. Meanwhile, a slight contact resistance exists between particles, so that the conductivity is made smaller than the conductivity of a lump of graphite.

[0003]

On the other hand, there is a new carbon material known as a name of carbon nanotube developed in recent years. The new carbon material has a fiber structure that one or several cylinders that the graphite-shaped carbon atom surface is rounded are arranged in a nested state, and the length is within the range from several  $\mu\text{m}$  to several tens  $\mu\text{m}$ , and the diameter is very small such as the order of nanometer. Carbon fibers with a diameter of microns or more have been known from long ago, though tubes with a diameter of the order of nanometer are disclosed in the report in 1991, "Nature Journal, 1991, Vol. 354, pp. 56 to 58". The electrical characteristics of the carbon nanotube are described in Physical Review Journal, "Physical Review Letter Journal, 1992, Vol. 68, pp. 1579 to 1581". However, this material is not isolated perfectly, so that the actual conductivity is not made clear. Therefore, whether a carbonaceous material

containing carbon nanotube functions as a conductivity giving agent for an electrode material of a battery or not is not made clear.

[0004]

[Problems that the Invention is to Solve]

The black mix for a battery electrode mentioned above is added with a conductivity giving agent because the positive electrode active material has not sufficient electron conductivity. However, the voltage of the battery drops during charge or discharge and the performance as a battery is not utilized fully. An object of the present invention is to solve the aforementioned problems and provide a black mix for a battery electrode that the internal resistance of the battery is reduced and a nonaqueous electrolytic battery using it.

[0005]

[Means of Solving the Problems]

The inventors, as a result of an earnest research, have obtained a nonaqueous electrolytic battery that a black mix for an electrode of a positive electrode battery is structured by using, as a carbon material for giving conductivity in the black mix for a battery electrode, carbon fibers having a new structure in a tube-shape, that is, a carbonaceous material containing a carbon nanotube or a carbonaceous material containing a carbon nanotube containing metallic ions, and the electron conductivity

thereof is reduced, and the internal resistance using it is reduced.

[0006]

Namely, the present invention is a black mix for a battery electrode characterized in that in the black mix for a battery electrode containing a positive electrode active material, a binder, and a conductivity giving agent, the conductive giving material is a carbonaceous material containing a carbon nanotube or a carbonaceous material containing a carbon nanotube containing metallic ions. In this case, the positive electrode active material is preferably manganese dioxide or lithium transition metal oxide. Further, according to the present invention, a nonaqueous electrolytic battery characterized in that it has a negative electrode for occluding the aforementioned black mix for a battery electrode and lithium and a nonaqueous solvent electrolyte is provided. In this case, the negative electrode for occluding lithium is preferably either of a carbonaceous material for intercalating or doping metallic lithium, lithium alloy, or lithium and a conductive macromolecular material.

[0007]

For manufacture of a carbon nanotube used in the present invention, a carbon material having a tube-shape tissue with a diameter of 50 Å to 100 Å prepared by causing DC charge between two graphite bars installed in a helium

atmosphere at pressure of 100 Torr to 500 Torr, that is, carbon nanotube or a one obtained by including metallic ions such as lithium using it as a raw material. The carbon nanotube obtained by this method is a mixture of, generally another carbon material, for example, a mixture with graphite or amorphous carbon. The existence ratio of the carbon nanotube and graphite can be decided by evaluation of an electron microscope. The inventors find that when the nanotube amount is expressed by a ratio of the volume ( $V_n$ ) obtained from the area of an electron microscope image to the total of the volume ( $V_n$ ) and the volume ( $V_g$ ) of the other graphite, that is,  $V_n/(V_n+V_g)$ , a carbonaceous material containing 30% or more carbon nanotube is particularly effective. When the carbon nanotube amount is less than 30%, the effect of the carbon nanotube does not appear clearly and a problem is imposed in the characteristic as a black mix for a battery electrode. To allow the carbon nanotube to contain a metallic element such as lithium, a lithium metal is mixed in the carbonaceous material containing carbon nanotube, which is prepared by the aforementioned method, in an inactive gas flow such as argon and heat-treated and reacted at 100°C to 200°C or a metallic compound such as lithium nitride or lithium carbonate is mixed and heat-treated and reacted at a maximum of about 400°C.

[0008]

Next, the positive electrode active material used in the present invention will be described. The black mix for a positive electrode of the present invention is characterized in that manganese dioxide on sale is used or  $\text{LiCoO}_2$ , which is a lithium transition metal oxide or a lithium oxide expressed by a chemical formula of  $\text{LiNiO}_2$ , is used and a black mix for a positive electrode that a carbon material containing a nanotube prepared by the aforementioned method or a carbon material containing a nanotube containing metallic ions and a binder are added and mixed with it is used. To manufacture  $\text{LiCoO}_2$  or  $\text{LiNiO}_2$ , a conventionally known method may be used. Namely, it is prepared by mixing and heat-treating carbonate of lithium, cobalt, and nickel or hydroxide in a predetermined amount as a start raw material. To it, a carbonaceous material of 1 wt% to 20 wt% containing a carbon nanotube or a carbon nanotube containing a metal such as lithium and a binder are added and mixed and a black mix for a positive electrode is prepared. When a carbon material containing a nanotube containing a metal is added to lithium oxide, the conductivity as an electrode is improved. The binder used here is properly selected from fluorine resin such as Teflon, starch, and thermoplastic resin which are conventionally used.

[0009]

Next, the negative electrode active material of the



present invention will be described. To structure a lithium primary battery, metallic lithium foil is used. To structure a lithium ion secondary battery, a pitch series graphitized carbon material, for example, mesocarbon microbeads (MCMB) manufactured by Osaka Gasu is used.

[0010]

An example of the constitution of a nonaqueous electrolytic battery prepared using a positive electrode and a negative electrode prepared by the aforementioned method will be explained by referring to Fig. 1. The battery is composed of a positive electrode 1, a negative electrode 4, a separator 3, a nonaqueous electrolyte, an anode can 2 as a current collector, and a cathode can 5. The separator 3 is not particularly limited and it may be woven cloth, fiber glass, or porous plastic resin. For example, a polyolefin series porous film is a thin film in a large area and the film strength and film resistance are proper respectively. As a support electrolyte,  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ , and  $\text{CF}_3\text{SO}_3\text{Li}$  may be cited. An organic solvent of an electrolyte may be a one which is generally used and for example, carbonate, chlorinated hydrocarbon, ether, ketone, and nickel may be cited. The battery is composed of components such as the current collector and insulating plate and they are not particularly limited.

[0011]

#### [Operation of the Invention]

The black mix for a battery electrode of the present invention is formed by adding and mixing a carbon material containing a carbon nanotube or a carbon material containing a carbon nanotube containing metallic ions as a conductivity giving agent with manganese dioxide and lithium transition metal oxide used as a positive electrode active material, so that the electron conductivity is improved. The unit of the carbon nanotube structure used in the present invention is a cylindrical structure that a graphite sheet is rounded and it is a highly complete structure containing no other structures other than a carbon six-membered ring. The central part of the carbon nanotube has a cylindrical hollow space with a diameter of several Å or more. The hollow cylindrical space is surrounded by a strong carbon six-membered ring, so that it has a highly stable structure and it is stable. The bonding in the axial direction is the same as the bonding of graphite, and the bonding power is extremely high, and the thermal stress and mechanical strength are also excellent. As the carbon nanotube structure shows, the electrical conductivity in the axial direction of the carbon nanotube is extremely satisfactory, so that although the diameter is the same as that of fine powder of nanometer size such as acetylene black, it can be expected to improve the conductivity. Therefore, the

resistance of the black mix for a battery electrode can be reduced and when it is incorporated into a battery, the initial voltage reduction at the time of discharge can be suppressed small.

[0012]

[Embodiments]

The embodiments of the present invention will be explained hereunder.

Embodiment 1

A carbon material containing a carbon nanotube is prepared by discharging a DC under the condition that a carbon bar with a diameter of 20 mm is used a cathode and a carbon bar with a diameter of 10 mm is used as an anode in a helium atmosphere at 500 torr. With respect to the rate of carbon nanotube to other graphite contained in the carbonaceous material, the volume ratio of nanotube to the whole amount is obtained from a transmission electron microscope as a carbon nanotube amount contained. The volume ratio of carbon nanotube used in the embodiment is about 60%. Electrolytic manganese dioxide (by Mitsui Kinzoku Kogyo) on sale of 0.94 g, Teflon powder of 0.01 g, and carbon material containing a carbon nanotube of 0.05 g are mixed and kneaded and processed in a sheet form with a thickness of 0.9 mm by a stainless steel round bar. The prepared sheet is punched in a circular form with a diameter of 17 mm and it is used as a positive electrode.

Metallic lithium is used as a negative electrode and by using a polypropylene separator and an electrolyte that perchlorate lithium is added to propylene carbonate so as to obtain a concentration of 1 mol/l, a coin-type cell as shown in Fig. 1 is prepared. The diameter of the coin-type cell is 23 mm and the thickness thereof is 2.0 mm.

[0013]

#### Embodiment 2

To make a carbon nanotube contain lithium, a carbon material containing a carbon nanotube prepared by the method described in Embodiment 1 is mixed with a lithium metal in an agate mortar in an inactive gas flow such as argon and heat-treated at 100°C to 200°C. Although the contained lithium amount is not clear, contained lithium is ascertained by the transmission electron microscope. Thereafter, manganese dioxide, Teflon powder, and carbon nanotube containing lithium are mixed at the same rate as that of Embodiment 1 and a sheet is prepared in the same way as with Embodiment 1. A coin-type cell is prepared in the same way as with Embodiment 1.

[0014]

#### Comparison Example 1

Manganese dioxide of 0.94 g and Teflon powder of 0.01 g in the same way as with Embodiment 1 and acetylene black (by Showa Denko) of 0.05 g instead of a carbon material containing a carbon nanotube are mixed and kneaded and

processed in a sheet form with a thickness of 0.9 mm by a stainless steel round bar. A coin-type cell is prepared in the same way as with Embodiment 1.

[0015]

For the sheets prepared in Embodiments 1 and 2 and Comparison Example 1, the specific resistance is obtained by the DC 4-probe method respectively. With respect to the internal resistance of the trial coin-type cells, an AC voltage of 10 mV is applied at 1 kHz and the real number part of the impedance at that time is decided as an internal resistance of the cells. The results are shown in Table 1 indicated below.

[0016]

[Table 1]

	Specific resistance of sheet ( $\Omega \cdot \text{cm}$ )	Internal resistance of coin-type cell ( $\Omega$ )
Embodiment 1	1.3	3.8
Embodiment 2	0.9	3.7
Comparison Example 1	2.3	4.5

[0017]

As Table 1 shows, the carbon nanotube and carbon nanotube containing metallic ions function effectively as a conductive giving agent. Further, the trial coin-type cells operate normally respectively.

[0018]

Embodiment 3

$\text{LiCoO}_2$  is prepared as a positive electrode active material. As raw materials, lithium carbonate of 1.06 mol and cobalt oxide as reduced  $\text{CoO}$  of 1.02 mol are weighed and mixed, temporarily baked at  $600^\circ\text{C}$  for 2 hours, and calcined in the air at  $900^\circ\text{C}$  for 12 hours. This oxide is crushed and classified so that the particle diameters of 95% are controlled within the range from 1  $\mu\text{m}$  to 10  $\mu\text{m}$  in the particle size distribution. With this raw material powder of 0.94 g, a carbon material containing a carbon nanotube of 0.05 g prepared by the method described in Embodiment 1 and Teflon powder of 0.01 g are mixed. A positive electrode black mix sheet is prepared in the same way as with Embodiment 1. As a negative electrode, mesocarbon microbeads (MCMB, manufactured by Osaka Gasu) of 0.99 g which is a pitch series graphitized carbon material and Teflon powder of 0.01 g are mixed and kneaded and a sheet is prepared in the same way as with the positive electrode. The positive electrode black mix sheet and negative electrode black mix sheet are punched in a circular form respectively as a positive electrode and a negative electrode. The electrolyte is prepared by dissolving  $\text{LiPF}_6$  with a concentration of 1 mol in a mixed solvent containing ethylene carbonate and diethyl carbonate of volume % of 50% and 50%. As a separator, a porous polypropylene film with a thickness of 25  $\mu\text{m}$  is used. Fig. 1 shows the constitution thereof.

[0019]

Comparison Example 2

Except that using graphite fine powder (by Mitsubishi Kasei) of 0.05 g instead of a carbon material containing a carbon nanotube, a positive electrode black mix sheet is prepared, a coin-type cell is assembled in the same way as with Embodiment 3. For the positive electrode black mix sheets prepared in Embodiment 3 and Comparison Example 2, the specific resistance is obtained by the DC 4-probe method respectively. The real number part of the impedance measured at a 100-mV signal voltage at a frequency of 1 kHz of the coin-type cells is decided as an internal resistance. The results are shown in Table 2 indicated below.

[0020]

[Table 2]

	Specific resistance of sheet ( $\Omega \cdot \text{cm}$ )	Internal resistance of coin-type cell ( $\Omega$ )
Embodiment 3	1.1	3.1
Comparison Example 2	3.6	8.3

[0021]

Also in the lithium ion secondary battery shown in Table 2, the effect of the conductivity giving agent of the carbon nanotube is clear.

[0022]

In Embodiment 3,  $\text{LiCoO}_2$  is used as a positive electrode

active material. However, even when  $\text{LiNiO}_2$ ,  $\text{LiMnO}_2$ , or  $\text{LiMn}_2\text{O}_4$ , which is expected as another positive electrode material of the lithium ion secondary battery is used, it is clear that the same effect as that of Embodiment 3 will be obtained. Further, in the aforementioned embodiment, an example that coin-type cells are used is shown. However, the shape of a battery is not particularly limited. In short, it is clear that the effect of the present invention will be obtained also in various shapes such as the square type, paper type, lamination type, and cylinder type.

[0023]

#### [Effects of the Invention]

As mentioned above, according to the present invention, since a black mix for a battery electrode using a carbon material containing a carbon nanotube or a carbon nanotube containing a metal as a conductivity giving agent is used, a nonaqueous electrolytic battery that the internal resistance is reduced and the battery voltage drop caused at the time of charge or discharge is improved can be provided. Therefore, the industrial value is extremely large.

#### [Brief Description of the Drawings]

Fig. 1 is a cross sectional view of an embodiment of a nonaqueous electrolytic battery of the present invention.

#### [Description of Numerals]